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(54) Ceramic material for facing metal dentures

(57) Ceramic materials with processing temperatures of around 770°C and heat expansion coefficients of 8-9 * 10^{-4} K^{-1}, or 16-17.5 * 10^{-5} K^{-1} for dentures made of low-temperature melting gold alloys and titanium alloys. These ceramic materials are composed of:
SiO_2, 4 to 15% by weight, Al_2O_5, 0.7 to 2.5 % by weight, B_2O_2 0 to 0.9 % by weight, Sb_2O_5, 0 to 0.5 % by weight, CaO_2, 0 to 2.5% by weight, BaO, 0 to 0.5% by weight, CaO, 7 to 12 % by weight, K_2O, 6 to 11 % by weight, Na_2O, 0.55 to 1.4 % by weight Li_2O, and 0.2 to 1.0 % by weight F_2.

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The invention concerns a ceramic material for facing metal dentures made of low-melting gold alloys or titanium with a processing temperature of 770°C +/- 70°C and a coefficient of thermal expansion alpha adjustable to the respective dental alloy between 20 and 500°C of $8 * 10^{-5}$ K^{-1}.

Ceramic layers have been applied to metal frames (crowns, bridges) as a kind of enameling for many years, in order to achieve a natural appearance of the dentures. In this case ceramic powders are applied as aqueous layers onto the metal frame and baked at high temperatures. In this case it is important that the baking temperature (processing temperature) of the ceramic material is at least 100°C under the solidification temperature of the material of the metal frame and the coefficient of thermal expansion of the ceramic material in the range of 20 to 500°C is slightly lower than that of the metal material, so that no cracks appear in the facing layer during the sintering and cooling.

Recently yellow gold alloys with gold contents between 70 and 85%, which have coefficients of thermal expansion between 15 and 17.5 10^{-5} K^{-1} are being used in dental technology. In addition to this titanium materials with coefficients of thermal expansion between 9 and $10 * 10^{-5}$ K^{-1} are being used. In addition, these gold alloys have solidification temperatures in the range of 870-940 °C, respectively in the case of titanium materials it is important to remain below the phase transformation temperature of around 880°C during the baking.

Ceramic materials, which cover such a wide range of the coefficients of thermal expansion and at the same time had a processing temperature in the area of around 700-840°c, have not been known up to now.

Therefore the object of the present invention was to develop a ceramic material for facing metal dentures made of low-melting gold alloys and titanium, which has a processing temperature of 880°C +/- 70°c, and a coefficient of thermal expansion between 20 and 500°C, which is adjustable to values between $8 * 10^{-5}$ and $17.5 * 10^{-5}$ K^{-1}.

This object is achieved according to the invention with an ceramic material, which is composed of $8 * 10^{-5}$ K^{-1}.

For gold alloys with coefficients of thermal expansion between 15 and 17.5% * 10^{-5} K^{-1} ceramic materials with the following composition have proven worthwhile: 60-68% by weight SiO_2, 10-15% by weight Al_2O_3, 0.7-1.5 % by weight B_2O_2, 0-0.5 % by weight Sb_2O_3, 0-2.5% by weight BaO, 0.1-0.5% by weight CaO, 9-12 % by weight K_2O, 9-11 % by weight Na_2O, 0.8-1.4 % by weight Li_2O, and 0.2-0.5 % by weight F_2.

The following compositions have proved to be particularly worthwhile: 82-85% by weight SiO_2, 12-15% by weight Al_2O_3, 0.8-1.2 % by weight B_2O_2, 0-0.2 % by

weight Sb_2O_3, 0-0.4 % by weight CaO_2, 0-0.1% by weight BaO, 0.2-0.4% by weight CaO, 9-11 % by weight K_2O, 9-11 % by weight Na_2O, 0.8-1.2 % by weight Li_2O, and 0.2-0.4 % by weight F_2.

For titanium and titanium alloys with coefficients of thermal expansion of 9-10 - $10^{-5} * K^{-1}$, ceramic material with the following compositions have proved to be worthwhile: 68-75% by weight SiO_2, 5-8% by weight Al_2O_3, 2-2.5 % by weight B_2O_2, 0.3-0.9 % by weight Sb_2O_3, 0-0.2 % by weight CaO_2, 1.5-2.5% by weight BaO, 0-0.3% by weight CaO, 7-11 % by weight K_2O, 6-10 % by weight Na_2O, 0.55-0.75 % by weight Li_2O, and 0.8-1.0 % by weight F_2.

Compositions with 70-72% by weight SiO_2, 5-7% by weight Al_2O_3, 2.1-2.4 % by weight B_2O_2, 0.4-0.6 % by weight Sb_2O_3, 1.8-2.2 % by weight BaO, 0-0.1% by weight CaO, 7-9 % by weight K_2O, 7-9 % by weight Na_2O, 0.55-0.75 % by weight Li_2O, and 0.8-1.0 % by weight F_2 have proved to be particularly worthwhile.

These ceramic material all have a processing temperature in the range between 700 and 840°C and may be adjusted to expansion coefficients between $8 * 10^{-5}$ and $17.5 * 10^{-5}$ K^{-1} in the range between 20 and 500°C.

The following examples are to explain the invention in greater detail:

1. A yellow dental alloy of 77% gold, 9% silver, 2% palladium, 4.3% platinum, 4.5% copper, 2% indium, and 1.2% zinc with a melting temperature of 900°C and a coefficient of thermal expansion of $16.5 * 10^{-5}$ K^{-1} was faced with a ceramic material of the composition 83.2% by weight SiO_2, 12.8% by weight Al_2O_3, 0.8% by weight B_2O_2, 0.2 % by weight Sb_2O_3, 0.2 % by weight CaO_2, 0.1% by weight BaO, 0.3% by weight CaO, 10.6 % by weight K_2O, 10.4 % by weight Na_2O, 1.1 % by weight Li_2O, and 0.3 % by weight F_2 at 770°C.

The ceramic material possessed a dilatometric softening point of 550°C, a glass point of 480°C and a coefficient of thermal expansion of $16.2 * 10^{-5}$ K^{-1}.

After the baking the ceramic material had a very good surface structure, which was below the usual level of the known ceramics, while the transparency was comparable with these materials.

The shear test according to draft DIN 13927 amounts to 34N/mm2. This value is in the average range in comparison with other baked alloys and baked metal ceramic materials.

The compound testing (qualitative adhesion test) according to ISO 8693.2 and draft DIN 13927 was passed excellently.

The hydrolysis resistance - 18 hours boiling in 4% acetic acid according to ISO 9693.2 and DIN 13927 or draft DIN 13927 produced practically no weighable loss of material. The gloss of the sample pieces is practically unchanged.

The bending strength according to DIN 13925 and ISO 9693.2 is 75 N/mm2 and thus with around 50% over the minimum bending strength of 50 N/mm2 required according to DIN and ISO.

2. A titanium bridge frame with a coefficient of thermal resistance of 9,8 * 10^{-5} K^{-1} was faced with a ceramic material of the composition 72.5% by weight SiO2, 4.5% by weight Al2O3, 2.5% by weight B2O2, 0.3 % by weight Sb2O3, 2.2 % by weight BaO, 7.5 % by weight K2O, 9.0 % by weight Na2O, 0.7 % by weight Li2O, and 0.8 % by weight F2 at 720°C

The ceramic material has a dilatometric softening point of 570°C, a glass point of 480°c, and a coefficient of thermal expansion of 8.3 x 10^{-5} K^{-1}.

After baking the transparency and the surface structure of the ceramic materials was impressively good and were over the usual level of the normal metal ceramic materials. The shear test according to draft DIN 13927 in the average was 30 N/mm2.

The bonding test (qualitative adhesion test) according to ISO 9693.2 and draft 13927 was passed excellently. The hydrolysis resistance, 15 hours boiling in 45 acetic acid according to ISO 9693.2 and DIN 13925 or draft DIN 13927 yielded practically no weighable loss of material. The gloss of the sample pieces was practically unchanged. The bending strength according to DIN 13927 and ISO 9693.2 was 85 N/mm2 and thus around 70% over the minimum bending strength of 50 N/mm2 required according to DIN and ISO.

Patent Claims

1. Ceramic material for facing metal dentures made of low-melting gold alloys or titanium, with a processing temperature of 770°C +/- 70°c, and an adjustable coefficient of thermal expansion between 20 and 500°C of 8 * 10^{-5} to 17.5 * 10^{-5} K^{-1}, wherein it is composed of 60-75% by weight SiO2, 4-15% by weight Al2O3, 0.7-2.5 % by weight B2O2, 0-0.9 % by weight Sb2O3, 0-0.5% by weight CaO2, 0-0.5% by weight BaO, 0.1-0.5% by weight CaO, 7-12 % by weight K2O, 8-11% by weight Na2O, 0.55-1.4 % by weight Li2O, and 0.2-1.0 % by weight F2.

2. The ceramic material according to Claim 1 for gold alloys with a coefficient of thermal expansion between 16 * 10^{-5} and 17.5 * 10^{-5} K^{-1}, wherein it is composed of 60-68% by weight SiO2, 10-15% by weight Al2O3, 0.7-1.5 % by weight B2O2, 0-0.5 % by weight Sb2O3, 0-2.5% by weight BaO, 0.1-0.5% by weight CaO, 9-12 % by weight K2O, 9-11 % by weight Na2O, 0.8-1.4 % by weight Li2O, and 0.2-0.5 % by weight F2.

3. The ceramic material according to Claim 2, wherein it is composed of 82-85% by weight SiO_2, 12-15% by weight Al_2O_3, 0.8-1.2 % by weight B_2O_2, 0-0.2 % by weight Sb_2O_3, 0-0.4 % by weight CaO_2, 0-0.1% by weight BaO, 0.2-0.4% by weight CaO, 9-11 % by weight K_2O, 9-11 % by weight Na_2O, 0.8-1.2 % by weight Li_2O, and 0.2-0.4 % by weight F_2.

4. the ceramic material according to Claim 1 for titanium and titanium alloys with a coefficient of thermal expansion between $8 * 10^{-5}$ and $8 * 10^{-5}$ K^{-1}, wherein it is composed of 68-75% by weight SiO_2, 4-8% by weight Al_2O_3, 2-2.5 % by weight B_2O_2, 0.3-0.9 % by weight Sb_2O_3, 0-0.2 % by weight CaO_2, 1.5-2.5% by weight BaO, 0-0.3% by weight CaO, 7-11 % by weight K_2O, 6-10 % by weight Na_2O, 0.55-0.75 % by weight Li_2O, and 0.8-1.0 % by weight F_2.

5. The ceramic material according to Claim 4, wherein it is composed of 70-74% by weight SiO_2, 4-7% by weight Al_2O_3, 2.1-2.4 % by weight B_2O_2, 0.4-0.5 % by weight Sb_2O_3, 1.8-2.2 % by weight BaO, 0-0.1% by weight CaO, 7-9 % by weight K_2O, 7-9 % by weight Na_2O, 0.55-0.75 % by weight Li_2O, and 0.8-1.0 % by weight F_2.